Thermochimica Acta, 197 (1992) 109–121
Elsevier Science Publishers B.V., Amsterdam

Enthalpies of formation for Group IV selenides ($GeSe_2$, $GeSe_2$(am), SnSe, $SnSe_2$, PbSe) by direct-combination drop calorimetry

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(Received 24 June 1991)

Abstract

We have determined the enthalpies of formation for $GeSe_2$(cr), $SnSe_2$(cr), SnSe(cr), and PbSe(cr) and for amorphous $GeSe_2$ using direct-combination drop calorimetry. Our results are as follows: $\Delta_f H^\circ_m$($GeSe_2$, cr, 298 K) $= -84.4 \pm 1.8$ kJ mol^{-1}, $\Delta_f H^\circ_m$($GeSe_2$, am, 298 K) $= -76.5 \pm 1.0$ kJ mol^{-1}, $\Delta_f H^\circ_m$($SnSe_2$, cr, 298 K) $= -126.9 \pm 1.6$ kJ mol^{-1}, $\Delta_f H^\circ_m$(SnSe, cr, 298 K) $= -93.8 \pm 3.3$ kJ mol^{-1}, and $\Delta_f H^\circ_m$(PbSe, cr, 298 K) $= -96.3 \pm 1.1$ kJ mol^{-1}. From our results for $\Delta_f H^\circ_m$($GeSe_2$, cr, 298 K) and $\Delta_f H^\circ_m$($GeSe_2$, am, 298 K), we have calculated the enthalpy of the process $GeSe_2$(am) $\rightarrow$ $GeSe_2$(cr) to be (-7.9 ± 2.1) kJ mol^{-1}.

INTRODUCTION

The chalcogenides of the Group IV elements represent a very interesting class of compounds. All are semiconductors and are of great interest for their electrical properties. The monoselenide compounds are isoelectronic with the Group V elements, and several of these compounds display temperature-dependent polymorphisms similar to those of the Group V elements [1]. The diselenides often form layered compounds with bonding properties similar to graphite [2]. Materials within the Ge–Se and Sn–Se systems readily form semiconducting glasses. Despite the great interest in these compounds, reliable thermodynamic values for these compounds are quite scarce. In this report, we present our experimental results for the standard enthalpies of formation for the crystalline selenides $GeSe_2$, $SnSe_2$, SnSe, and PbSe and for amorphous $GeSe_2$ as determined by direct-combination drop calorimetry.

The subject materials of this report are well characterized. Table 1 shows some of the physical properties of the known selenides of germanium, tin, and lead. The atmospheric-pressure phase diagrams for the

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TABLE 1

Physical properties of the selenides of germanium, tin and lead

Compound	Melting point (K)	Melting transition	Crystal structure type	Ref. for crystal structure
GeSe	948	Incongruent	GeS	1
$GeSe_2$	1013	Congruent	HT-GeS_2	25
SnSe	1153	Congruent	GeS	1
$SnSe_2$	948	Congruent	CdI_2	26
PbSe	1350	Congruent	NaCl	27

systems Ge–Se, Sn–Se, and Pb–Se are well established [3–5]. All of the compounds in Table 1 show narrow homogeneity ranges. GeSe and SnSe undergo λ-type phase transitions to high-temperature polymorphs at 933 K and 813 K, respectively. The high-temperature polymorphs of GeSe and SnSe have NaCl-type and TlI-type structures, respectively [6,7]. Karakhanova et al. [8] have suggested the existence of a low temperature modification of $GeSe_2$ in analogy with GeS_2 but this has evidently not gained acceptance. Numerous studies have addressed the enthalpies of formation of these compounds [9–24], but most have employed indirect experimental methods usually at high temperatures.

EXPERIMENTAL

Table 2 shows the specifications of our starting materials. Tin and lead were used as received. Germanium was crushed and sized to -200 mesh (< 75 μm). The selenium shot was crystallized by annealing under vacuum at about 500 K for 48 h. It was then crushed and sized to -100 mesh (< 150 μm) immediately before use. Powder X-ray diffraction patterns

TABLE 2

Specifications of starting materials

Element	Source	Catalog number	Purity	Form
Ge	Sylvania	–	Less than 1 part in 10^{10} contaminant	Crystalline ingot
Sn	Johnson Matthey	11013	99.999% [a]	Crystalline powder, -100 mesh (<150 μm)
Pb	Johnson Matthey	12716	99.999% [a]	Crystalline powder, $-100+200$ mesh (<150 μm, >75 μm)
Se	Johnson Matthey	10603	99.999% [a]	Amorphous shot, 1–3 mm

[a] With respect to metallic contaminants.

were collected on the selenium amorphous material and on samples which had been annealed for 24 and 48 h. All of the reaction mixtures were formulated stoichiometrically.

We made a set of five to seven samples for each of the mixtures which we investigated calorimetrically. For each sample, the elemental reagents were mixed together in a dry agate mortar, pelletized, and sealed in a fused silica capsule under vacuum. Each sample was then dropped into a Calvét-type double calorimeter which is described in detail in a previous publication [28] at a temperature of 1042 ± 1 K. The calorimeter was calibrated by dropping slugs of $> 99.99\%$ gold into the calorimeter and relating the resulting heat effects to the known heat content of that metal [29]. For the present experiments, the receiving vessel inside the calorimeter was a gold crucible. One of the samples from each set was examined by powder X-ray diffraction and scanning electron microscopy (SEM) with X-ray microprobe analysis after it was dropped once. For $GeSe_2$ and $SnSe_2$, we used the initial drop on each capsule to measure $\Delta_{r1}H$, the enthalpy of the process

$$\begin{aligned}&\mathrm{A(cr)} + 2\mathrm{Se(cr)} + k\mathrm{SiO_2(am)}\ (T = 296 \pm 2\ \mathrm{K}) \rightarrow\\ &\quad \mathrm{ASe_2(liq)} + k\mathrm{SiO_2(am)}\ (T = 1042\ \mathrm{K}) \qquad (1)\end{aligned}$$

where A represents Ge or Sn, $k = n(\mathrm{SiO_2})/n(\mathrm{ASe_2})$, and T is temperature. The value of k, which represents the amount of fused silica in the capsule and which varied from sample to sample, is arbitrary because the capsule material did not react. After each drop, we annealed the capsules containing $GeSe_2$ at about 960 K for 2 h in order to crystallize the compound. We dropped the reacted samples again in order to measure $\Delta_{r2}H$, the enthalpy of the process

$$\begin{aligned}&\mathrm{ASe_2(cr)} + k\mathrm{SiO_2(am)}\ (T = 296 \pm 2\ \mathrm{K}) \rightarrow\\ &\quad \mathrm{ASe_2(liq)} + k\mathrm{SiO_2(am)}\ (T = 1042\ \mathrm{K}) \qquad (2)\end{aligned}$$

We prepared amorphous samples of $GeSe_2$ by placing the capsules in a furnace set at about 1050 K and quenching them in room-temperature water. These capsules were dropped in order to measure $\Delta_{r3}H$, which is the enthalpy of the process

$$\begin{aligned}&\mathrm{GeSe_2(am)} + k\mathrm{SiO_2(am)}\ (T = 297 \pm 2\ \mathrm{K}) \rightarrow\\ &\quad \mathrm{GeSe_2(liq)} + k\mathrm{SiO_2(am)}\ (T = 1042\ \mathrm{K}) \qquad (3)\end{aligned}$$

The sample material was remelted and quenched between each drop.

Because our results for $GeSe_2$ were in poor agreement with previous work, we performed a set of additional experiments to verify that the heat effects that we observed corresponded to the processes above. In order to confirm that no reaction ocurred before the samples were dropped, an unreacted pellet of Se + Ge also was examined using SEM. In order to verify that the annealing procedure was effective in producing the desired crystalline product, after two of the $GeSe_2$ capsules were dropped for the last time, we annealed one for 2 h and the other for 12 h. A third capsule was quenched, so that we could confirm that we had obtained amorphous $GeSe_2$ for process 3. These three capsules were examined using powder X-ray diffractometry.

For SnSe and PbSe, the compound remained solid at the calorimeter temperature. The initial drops were used to measure $\Delta_{r4}H$, the enthalpy of the process

$$\mathrm{B(cr)} + \mathrm{Se(cr)} + k\mathrm{SiO_2(am)}\ (T = 296 \pm 1\ \mathrm{K}) \rightarrow \\ \mathrm{BSe(cr)} + k\mathrm{SiO_2(am)}\ (T = 1042\ \mathrm{K}) \qquad (4)$$

where B represents Sn or Pb. Subsequent drops were used to measure $\Delta_{r5}H$, which is the enthalpy of the process

$$\mathrm{BSe(cr)} + k\mathrm{SiO_2(am)}\ (T = 296 \pm 1\ \mathrm{K}) \rightarrow \\ \mathrm{BSe(cr)} + k\mathrm{SiO_2(am)}\ (T = 1042\ \mathrm{K}) \qquad (5)$$

RESULTS

All of the SEM analyses showed that only a single phase was present in each sample. The SEM analysis of the unreacted pellet of $GeSe_2$ showed only two phases which corresponded to the reactant materials.

The powder X-ray diffraction pattern collected on amorphous selenium over the range $4.44\ \text{Å} \geqslant d \geqslant 1.005\ \text{Å}$ revealed only two extremely broad features, one centered at 3.4 Å and the other at 1.7 Å. The powder patterns for the two annealed selenium samples were essentially identical and showed excellent agreement with powder patterns collected from the hexagonal crystalline material [30]. We concluded that our selenium starting material crystallized completely within 24 h at 500 K. The powder patterns collected from the PbSe and the $GeSe_2$(cr) sample which was dropped once showed excellent agreement with patterns collected by previous researchers for those compounds [31,32]. The powder pattern for SnSe was consistent with that of the low temperature polymorph as determined by Calvert [33] from the crystal structure proposed by Avilov et al. [33b]. The powder pattern for $SnSe_2$ showed good agreement with the powder pattern presented by Karakhanova et al. [15] for that compound. None of the patterns collected on these samples displayed features corresponding to the starting materials or to their oxides.

The powder X-ray diffraction patterns for the two annealed samples of $GeSe_2$ were also in excellent agreement with that calculated by Calvert [32], from the crystal structure proposed in ref. 24. Because these patterns were taken at the same time, that is under very similar conditions, and because there was no significant difference between the two patterns, we

TABLE 3

Results for the enthalpy of formation of $GeSe_2$(cr) at 297 K

Sample no.	$n(GeSe_2)$ (kJ mol^{-1})	$n(SiO_2)$ (mmol)	$\Delta_{r1}H$ (J)	$\Delta_{r2}H$ (J)	s [a]	$\Delta_f H^\circ_m$ (J)	s [a]
24	4.248	26.33	1244.2	1593.9		−83.5	
				1601.6			
				1600.3			
				1599.4			
				1598.8 [b]	3.4		
25	4.372	28.03	1319.5	1699.9		−86.8	
				1698.2			
				1696.4			
				1701.9			
				1699.1 [b]	2.3		
27	4.422	26.57	1256.6	1627.9		−84.5	
				1628.0			
				1632.0			
				1633.9			
				1630.5 [b]	3.0		
28	4.402	25.81	1219.2	1579.3		−82.7	
				1593.5			
				1587.3			
				1572.0			
				1583.0 [b]	9.4		
						−84.4 [b]	1.8

[a] s is the standard deviation of a population.

[b] Mean value.

conclude that the annealing procedure was effective in producing the pure crystalline compound in 2 h. The pattern collected from the sample which was dropped once showed the same relative intensities within the pattern as the annealed samples, but different absolute intensities. (The difference in absolute intensities is not surprising because the unannealed sample was collected at a different time using different instrumental settings.) The similarities between the annealed and unannealed samples suggest that the capsules cooled slowly enough after each drop to crystallize most or all of the material. The powder X-ray diffraction pattern of the quenched sample, which was collected at the same time as the annealed samples over the range 8.8 Å $\geqslant d \geqslant$ 2.15, displayed two extremely broad features at $d = 6.3$ Å and $d = 3.1$ Å and no sharp peaks.

Table 3 shows calorimetric results for $GeSe_2$(cr). The value for $\Delta_f H^\circ_m$($GeSe_2$, cr, 297 K) was calculated as $(\Delta_{r1}H - \langle \Delta_{r2}H \rangle)/n(GeSe_2)$. Table 4 shows analogous data for $\Delta_f H^\circ_m(GeSe_2$, am, 298 K) $= (\Delta_{r1}H - \langle \Delta_{r3}H \rangle)/n(GeSe_2)$. Table 5 shows calorimetric results for $\Delta_f H^\circ_m$($SnSe_2$, cr,

TABLE 4

Results for the enthalpy of formation of amorphous $GeSe_2$ at 298 K

Sample no.	$n(GeSe_2)$ (mmol)	$n(SiO_2)$ (mmol)	$\Delta_{r1}H$ (J)	$\Delta_{r3}H$ (J)	s [a]	$\Delta_f H^\circ_m$ (kJ mol^{-1})	s [a]
24	4.248	26.33	1244.2	1570.7		−76.4	
				1568.6			
				1567.6			
				1567.9			
				1568.7 [b]	1.4		
25	4.372	28.03	1319.5	1659.9		−77.8	
				1658.6			
				1661.0			
				1659.8 [b]	1.2		
27	4.422	26.57	1256.6	1592.5		−75.5	
				1590.6			
				1589.2			
				1589.8			
				1590.5 [b]	1.4		
28	4.402	25.81	1219.2	1552.6		−76.3	
				1558.7			
				1553.5			
				1556.1			
				1555.2 [b]	2.8		
						−76.5 [b]	1.0

[a,b] See footnotes to Table 3.

295 K). Both $GeSe_2$ and $SnSe_2$ melted during drops and the sample material settled in the capsule as the experiments proceeded. $SnSe_2$ retained the appearance of liquid throughout the experiments; $GeSe_2$ took on a granular appearance during annealing. $GeSe_2$ had a lusterous golden surface and appeared dark red when held up to light. It ground to a sticky, dull orange powder. The powder of the amorphous material was slightly more red than the crystalline material and was less sticky. $SnSe_2$ was dark bluish gray with a slight luster, much like graphite.

Table 6 shows calorimetric results for SnSe where $\Delta_f H^\circ_m$(SnSe, cr, 296 K) $= (\Delta_{r4}H - \langle \Delta_{r5}H \rangle / n(\text{PbSe})$. Table 7 shows results for $\Delta_f H^\circ_m$(PbSe, cr, 296 K). Both SnSe and PbSe melted during the initial drop, but SnSe showed signs of crystal growth by the time it was examined at room temperature. Neither compound showed significant change after the first drops. Both of these solids looked similar to $SnSe_2$.

DISCUSSION

For the monoselenides, our X-ray diffraction results unambiguously identified our product materials as the same as those synthesized by other

TABLE 5

Data for the determination of the heat of formation of $SnSe_2$ at 295 K

Sample no.	$n(SnSe_2)$ (mmol)	$n(SiO_2)$ (mmol)	$\Delta_{r1}H$ (J)	$\Delta_{r2}H$ (J)	s [a]	$\Delta_f H^\circ_m$ (kJ mol^{-1})	s [a]
1	4.423	28.53	1364.2	1925.0		−127.2	
				1931.6			
				1925.7			
				1925.4			
				1926.9 [b]	3.1		
2	4.127	23.60	1125.6	1653.1		−127.8	
				1649.2			
				1647.3			
				1661.9			
				1652.9 [b]	6.5		
3	4.037	24.30	1157.2	1675.6		−128.2	
				1668.0			
				1664.3			
				1690.6			
				1675.2			
				1674.7 [b]	10.1		
4	3.928	22.32	1075.0	1567.1		−124.6	
				1549.9			
				1570.9			
				1569.5			
				1564.3 [b]	9.8		
						−126.9 [b]	1.6

[a,b] See footnotes to Table 3.

researchers. For the diselenides, this was less straightforward; alternate patterns exist for both $GeSe_2$ and $SnSe_2$ for our experimental conditions [8,34–36]. The variation in the X-ray diffraction patterns of $GeSe_2$ has been ascribed to differences in the stacking order of the distorted hexagonal layers within the crystal structure [15]. Because the bonding between layers is thought to be rather weak [2], we assert that the enthalpy differences between these different phases are negligible when compared to the enthalpy of formation.

Table 8 shows a comparison between the enthalpy results of this study and the results of previous investigators. We have assumed that the difference between the enthalpy of formation at the experimental temperature (e.g. 295 K for SnSe) and at 298 K is negligible. In Table 8, we have consistently quoted the third law derivation of the heat of formation from the Gibbs energies of related reactions.

As previously stated, we were disturbed by the poor agreement between our results for $\Delta_f H^\circ_m(GeSe_2$, cr, 298 K) and for $\Delta_f H^\circ_m(GeSe_2$, am, 298 K)

TABLE 6

Results for the enthalpy of formation of SnSe at 296 K

Sample no.	n(SnSe) (mmol)	$n(SiO_2)$ (mmol)	$\Delta_{r4}H$ (J)	$\Delta_{r5}H$ (J)	s [a]	$\Delta_f H^\circ_m$ (kJ mol^{-1})	s [a]
3	5.265	23.86	883.4	1394.6		−96.6	
				1395.0			
				1391.4			
				1388.3			
				1392.3 [b]	3.1		
4	5.313	20.48	751.6	1234.3		−88.8	
				1228.7			
				1217.5			
				1213.7			
				1223.5 [b]	9.6		
5	5.467	20.92	726.4	1241.3		−94.7	
				1244.8			
				1248.4			
				1240.8			
				1243.8 [b]	3.5		
6	5.155	21.08	760.1	1263.5		−96.5	
				1289.4			
				1239.8			
				1237.5			
				1257.5 [b]	24.3		
7	5.899	23.90	893.6	1426.9		−90.4	
				1434.2			
				1422.1			
				1425.4			
				1427.2 [b]	5.1		
8	5.978	21.00	709.0	1275.3		−95.6	
				1288.8			
				1284.0			
				1274.4			
				1280.6 [b]	7.0		
						−93.8 [b]	3.3

[a,b] See footnotes to Table 3.

and the results of previous researchers. Although our results for $GeSe_2$(cr) are in marginal agreement with Irene and Weidemeier [9], the agreement with both Chirulli and Piacente [10] and O'Hare [11] is poor. The fact that O'Hare's results for both $\Delta_f H^\circ_m(GeSe_2$, cr, 298 K) and $\Delta_f H^\circ_m(GeSe_2$, am, 298 K) are about 20% more negative than ours suggests a systematic error in one determination or the other. The fact that our results for other compounds are in good agreement with literature values suggests that the systematic error is in O'Hare's determination. It might be suggested that

TABLE 7

Data for the determination of the heat of formation of PbSe at 296 K

Sample no.	n(PbSe) (mmol)	n(SiO_2) (mmol)	$\Delta_{r4}H$ (J)	$\Delta_{r5}H$ (J)	s [a]	$\Delta_f H_m^\circ$ (kJ mol^{-1})	s [a]
2	4.101	18.01	630.4	1017.5		−94.9	
				1017.8			
				1023.1			
				1019.5 [b]	3.1		
3	5.372	25.02	888.8	1410.9		−96.5	
				1406.5			
				1404.1			
				1407.2 [b]	3.4		
4	5.184	23.35	811.2	1312.5		−97.4	
				1319.9			
				1315.7			
				1316.0 [b]	3.7		
5	5.321	19.27	616.4	1130.2		−96.6	
6	5.090	18.37	582.2	1073.6		−96.8	
				1076.2			
				1075.0			
				1074.9 [b]	1.3		
						−96.3 [b]	1.1

[a,b] See footnotes to Table 3.

the enthalpy differences between our result and O'Hare's for $\Delta_f H_m^\circ$($GeSe_2$, cr, 298 K) might arise from the fact that we were studying different phases of $GeSe_2$, i.e. phases with differing stacking orders. The disagreement between our results and O'Hare's for $\Delta_f H_m^\circ$($GeSe_2$, am, 298 K) tends to argue against that possibility.

In our opinion, the uncertainty in the result of Karakhova et al. for $\Delta_f H_m^\circ$(SnSe, cr, 298 K) [15] is unrealistic small for a method which makes use of dissociation pressure measurements. Their quoted uncertainty in $\Delta_f H_m^\circ$(SnSe, cr, 298 K) should be compared with the uncertainty in their value for $\Delta_f H_m^\circ$($SnSe_2$, cr, 298 K). The authors also used estimated values for the heat capacities of the components in order to correct their high-temperature results to 298 K. Hajiev's results for both $\Delta_f H_m^\circ$(SnSe, cr, 298 K) and $\Delta_f H_m^\circ$(PbSe, cr, 298 K) are based on the technique of direct-combination bomb calorimetry [16]. Since Hajiev himself states that the technique is not very reliable if the binary system forms more than one compound, his value for $\Delta_f H_m^\circ$(SnSe, cr, 298 K) [16] cannot be accepted without some reservation.

Our results for $\Delta_f H_m^\circ$(PbSe, cr, 298 K) are in poor agreement with the findings of Hajiev [16] and of Shamsuddin and Misra [23]. Hajiev's result

TABLE 8

Comparison of presently reported results for enthalpies of formation with literature values

Compound	$\Delta_f H^\circ_m$(298 K) (kJ mol^{-1})	Method	Ref.
$GeSe_2$(cr)	−91 ± 8	Knudsen effusion	9
	−114 ± 17	Torsion effusion	10
	−102.2 ± 2.6	F-bomb calorimetry	11
	−84.4 ± 1.8	Direct-combination calorimetry	This work
$GeSe_2$(am)	−90 ± 5	F-bomb calorimetry	12
	−76.5 ± 1.0	Direct-combination calorimetry	This work
SnSe	−91 ± 4 [a]	Direct-combination calorimetry	13
	−90 ± 7	Knudsen effusion	14
	−89.5 ± 0.4	Dissociation pressure	15
	−90.8 ± 0.8	Direct-combination bomb calorimetry	16
	−95 ± 2	E.m.f. measurement	17
	−94 ± 3	Direct-combination calorimetry	This work
$SnSe_2$	−121 ± 8	Enthalpy of $H_2(g) + SnSe_2(s) \rightarrow SnSe(s) + H_2Se(g)$	18
	−153 ± 9	Dissociation pressure	15
	−124.7 ± 1.2	E.m.f. measurement	17
	−109 ± 21	Dissociation pressure	19
	−126.9 ± 1.6	Direct-combination calorimetry	This work
PsSe	−100 ± 8	E.m.f. measurement	20
	−102 ± 8	Dissociation pressure	21
	−99 ± 4	E.m.f. measurement	22
	−105.0 ± 1.4	Direct-combination bomb calorimetry	16
	−102 ± 1	Quantitative thermal analysis	23
	−101 ± 5	Extrapolation from HT calorimetric data	24
	−96 ± 1	Direct-combination calorimetry	This work

[a] The uncertainty in this result was recalculated by the authors as the standard deviation of a population from the final results for the individual samples.

[16] is based on the technique of direct-combination bomb calorimetry which seems unreliable because the components do not react completely. Shamsuddin and Misra's result for $\Delta_f H^\circ_m$(PbSe, cr, 298 K) [23] is based on the technique of quantitative thermal analysis (QTA) where the sample reacted marginally at 423 K and to completion above 490 K. Although Shamsuddin and Misra provide high-temperature e.m.f. results to support their value derived from QTA [23], the uncertainty of their preferred result seems somewhat optimistic. Figure 1 shows the trends in the enthalpies of formation of the Group IV selenides from germanium to lead based on our results and the result of O'Hare et al. [37] for $\Delta_f H^\circ_m$(GeSe, cr, 298 K).

From our results for $\Delta_f H^\circ_m$($GeSe_2$, cr, 298 K) and $\Delta_f H^\circ_m$($GeSe_2$, am, 298 K), we have calculated the enthalpy of the transition $GeSe_2$(am) → $GeSe_2$(cr) to be)7.9 ± 2.1 kJ mol^{-1}. We have calculated the uncertainty as the square root of the sum of the squares of the contributing uncertainties.

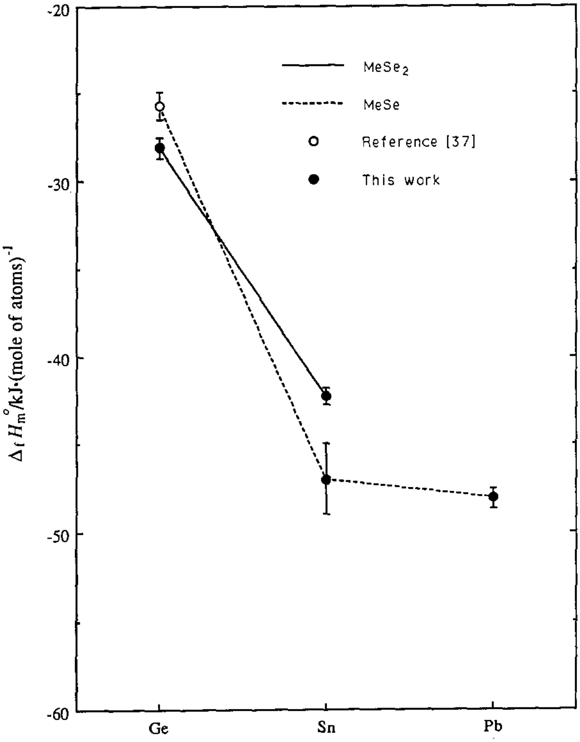

Fig. 1. Comparison of the enthalpies of formation of the selenides of germanium, tin and lead.

In analogy with the definition for the enthalpy of fusion, we define the enthalpy of divitrification, $\Delta_{\mathrm{dev}}H_{\mathrm{m}}^{\circ}(\mathrm{GeSe_2})$, as the enthalpy change for the transition: $\mathrm{GeSe_2(cr)} \rightarrow \mathrm{GeSe_2(am)}$. Therefore, $\Delta_{\mathrm{dev}}H_{\mathrm{m}}^{\circ}(\mathrm{GeSe_2}, 298\ \mathrm{K}) = 7.9 \pm 2.1\ \mathrm{kJ\ mol^{-1}}$. Table 9 shows a comparison between this result and related literature values. The difference between $\Delta_{\mathrm{dev}}H_{\mathrm{m}}^{\circ}(\mathrm{GeSe_2}, 298\ \mathrm{K})$ and $\Delta_{\mathrm{fus}}H_{\mathrm{m}}^{\circ}(\mathrm{GeSe_2}, 1013\ \mathrm{K})$ represents enthalpy difference between the liquid and the glass and likely shifts in $\Delta_{\mathrm{dev}}H_{\mathrm{m}}^{\circ}(\mathrm{GeSe_2})$ and $\Delta_{\mathrm{fus}}H_{\mathrm{m}}^{\circ}(\mathrm{GeSe_2})$

TABLE 9

Comparison of presently reported result for the enthalpy of devitrification of $\mathrm{GeSe_2}$ with literature values

$\Delta_{\mathrm{dev}}H_{\mathrm{m}}^{\circ}(\mathrm{GeSe_2}$, 298 K) (kJ mol^{-1})	Technique	Ref.	$\Delta_{\mathrm{fus}}H_{\mathrm{m}}^{\circ}(\mathrm{GeSe_2}$, 1013 K) (kJ mol^{-1})		Ref.
12 ±4	F-bomb Calorimetry	12	26.9	Calculated value	3
7.9±2.1	Drop calorimetry	This work	24	QTA	34
			26 ±3	QTA	38

over the large temperature difference. The result of O'Hare et al. [12] also suggest these effects but to a lesser degree.

ACKNOWLEDGMENTS

This work was supported by grants NSF-CHE8700937 and NSF-CHE9014789, and has also benefitted from the NSF-MRL grant. We are indebted to Dr. A.M. Davis who carried out the SEM examination of our samples.

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